

# Electronic Characteristics of Hydrogen-Saturated Silicon Clusters Deposited on Silicon Substrates

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Adsorption structures and electronic characteristics of hydrogen-saturated silicon clusters deposited on silicon substrates have been investigated by scanning tunneling microscopy and spectroscopy (STM/STS). Two types of hydrogen-saturated Si-cluster ions ( $\text{Si}_n\text{H}_x^+$ ,  $n=6$ ,  $x=13$  and  $n=8$ ,  $x=19$ ) grown in an ion trap have been selectively deposited on silicon substrates at room temperature with kinetic energies of 6 and 12 eV. Different adsorption structures were observed depending on the cluster type; the chain-like clusters ( $n=8$ ) formed an array with two-fold symmetry along straight surface steps. STS spectra measured over isolated clusters showed significant conductance variations dependent on the cluster structure due to resonance tunneling by cluster molecular levels. The results demonstrate that electronic properties of deposited clusters depend on the cluster type and the local arrangement.

Key words: Hydrogenated Si clusters, silicon, physical adsorption, tunneling

## 1. INTRODUCTION

Properties of structure-controlled semiconductor clusters on solid surfaces are of great interest because variety of physical characteristics is tunable with size and structure of clusters. These studies may also give important insight to new generation of electronic elements whose characteristics are affected by the discrete nature of electron states leading to size-dependent and nonlinear electrical behavior.

Hydrogen-saturated silicon clusters ( $\text{Si}_n\text{H}_x$ ) having two hydrogen atoms per each Si-atom seem to be promising constructive blocks in nanoelectronics since they have well-defined and stable structures.[1, 2] Recently, a structure-controlled growth of the  $\text{Si}_n\text{H}_x^+$  cluster ions in an ion trap has been achieved.[3, 4] The development of the cluster generation technique allows us to deposit the clusters with certain structures under precise control of the deposition energy. We have already reported on nondestructive deposition of the hydrogenated-silicon cluster ions  $\text{Si}_6\text{H}_{13}^+$  on Si(111)-(7x7) surfaces with a kinetic energy of 18 eV at room temperature where a partial ordering of the clusters near step edges and domain boundaries was observed.[5]

In this paper, we have studied adsorption structures and local electronic characteristics of hydrogen-saturated silicon clusters  $\text{Si}_6\text{H}_{12}$  and  $\text{Si}_8\text{H}_{18}$  deposited on Si(111)-(7x7) surfaces at a sub-monolayer coverage. We show that adsorption and

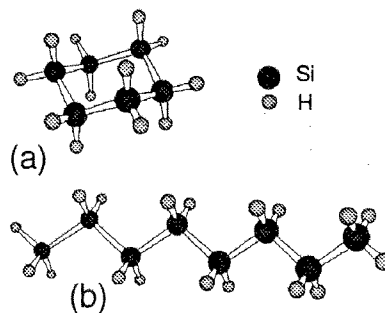


Figure 1: Calculated structures of neutral  $\text{Si}_n\text{H}_x$  clusters with  $n=6$ ,  $x=12$  (a) and  $n=8$ ,  $x=18$  (b).

electronic characteristics depend on the cluster type.

## 2. EXPERIMENTAL

Hydrogenated-silicon cluster ions ( $\text{Si}_n\text{H}_x^+$ ) were grown from silane ( $\text{SiH}_4$ ) gas with  $\text{H}_2$  ambient gas in an ion trap.[3]  $\text{Si}_n\text{H}_x^+$  ions generated were confined to the cage of the ion trap and were grown to the certain structure through reactions with  $\text{SiH}_4$  molecules and radicals. The grown cluster ions were mass-selectively ejected from the ion trap for deposition. Mass spectra measured at a substrate position showed that about 90% of the total ion beam consisted of selected cluster ions. The calculated structures of hydrogen-saturated clusters with  $n=6$ ,  $x=12$  (ring-like) and  $n=8$ ,  $x=18$  (chain-like) are shown in

Fig.1.

The cluster ions were deposited on the Si(111)-(7x7) substrate (n-type, 0.001  $\Omega$  cm, As doped) at room temperature with the kinetic energy of 6 and 12 eV (FWHM = 2 eV) controlled by applying retarding voltages to the substrate. After the deposition the samples were immediately transferred to a STM operating at residual pressure of  $\sim 5 \times 10^{-9}$  Pa. The STM/STS characterizations were performed in constant current mode at tunneling currents of 0.1 - 0.5 nA and sample biases of -1.5 - 2.5 V. Sharp tungsten tips were prepared *in-situ* with field-ion microscopy to have one atom on the top. Differential conductance ( $dI/dV$ ) spectra were calculated from I-V characteristics measured at constant tip-sample separation and normalized by an exponential function fitting the measured ( $I/V$ ) spectrum.

### 3. CLUSTER ADSORPTION

#### 3.1. $Si_6H_{12}$ adsorption structure

Figure 2 shows filled-state STM images of the Si(111)-(7x7) surface deposited with  $Si_6H_{13}^+$  ions at 12 eV. Deposited clusters are seen as bright circular dots on the large terrace with the (7x7) surface reconstruction. The cluster density is  $\sim 10^{12} cm^{-2}$ , which agrees the deposited amount estimated from the cluster-ion beam current. Evaluation of STM images shows that clusters are observed more often (about 70%) in brighter, faulted halves of the (7x7) unit cell. At high cluster density a coupling of the clusters is observed.

As seen from a detailed image in Fig.2(b), the surface reconstruction does not show significant changes around the isolated clusters due to weak interaction between the clusters and the surface. The weak clusters-substrate interaction is also in line with the observation that accumulation of the clusters deposited at 18 eV takes place at step edges resulting from high cluster mobility.[5] According to the calculations of the cluster structure, the ring-like  $Si_6H_{12}$  is the most stable with the lowest formation energy, when all the Si atoms are saturated by two hydrogen atoms.[2] As the neutral  $Si_6H_{13}$  cluster is unstable, the deposited ion is converted to the neutral  $Si_6H_{12}$  cluster and a hydrogen atom on the surface. This conversion is consistent with

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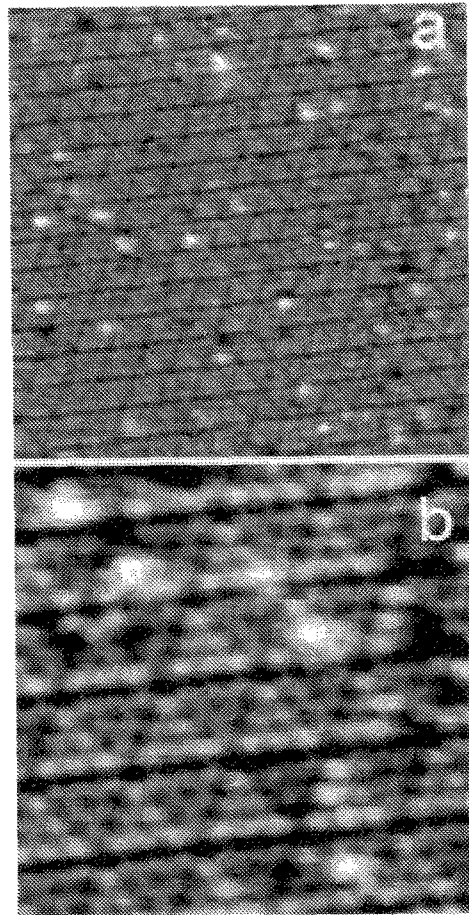


Figure 2: Filled-state STM images of the Si(111)-(7x7) surface deposited with  $Si_6H_{13}^+$  ions at 12 eV. The image size is (a) 38 nm and (b) 14 nm.

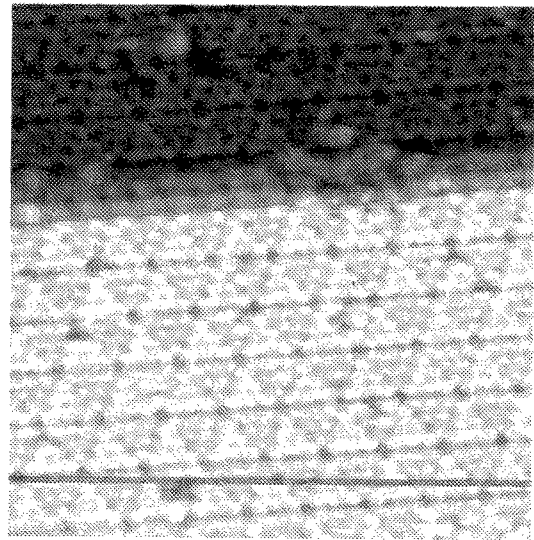


Figure 3: Filled-state STM images ( $20 \times 20 nm^2$ ) of an (2x1) array of  $Si_8H_{18}$  clusters deposited at 6 eV.

the fact that dark adatoms are observed near the cluster since hydrogen terminates a dangling bond of the surface atom as similar as that after low hydrogen exposure of the Si(111)-(7x7) surface.[6] The fact that the distance between a cluster and a dark adatom is as large as 1-2 unit cells indicates low mobility of clusters deposited at 12 eV.

### 3.2. $\text{Si}_8\text{H}_{18}$ cluster ordering

Deposition of  $\text{Si}_8\text{H}_{18}^+$  cluster ions shows pronounced difference in cluster ordering on the surface. We see clusters on flat terraces and at a step edge as shown in Fig.3. Dark adatoms seen in the image indicates conversion of the ion to a neutral  $\text{Si}_8\text{H}_{18}$  in a similar way as that occurs for  $\text{Si}_6\text{H}_{13}^+$  clusters. However, in contrast to  $\text{Si}_6\text{H}_{12}$ , the clusters are arranged at the straight step edge and they make an array with two-fold symmetry. The cluster separation is  $\sim 1.20$  nm along the step and 0.70 nm in the perpendicular direction. By annealing at 600°C (above hydrogen desorption temperatures) the ordered structure disappeared and large Si islands were formed due to destruction of clusters and coalescence of Si atoms of clusters, which confirms that the ordering is actually due to the deposited clusters. While the neutral  $\text{Si}_6\text{H}_{12}$  cluster consists of a ring of 6 Si-atoms (Fig.1(a)), the stable neutral  $\text{Si}_8\text{H}_{18}$  cluster is a chain of 8 Si-atoms with  $sp^3$ -bonding (Fig.1(b)) and, thus, can be adsorbed with a specific orientation at step edges. Therefore, the difference in the cluster type results in the observed adsorption structures, and leads to differences in electronic characteristics shown below.

## 4. ELECTRONIC CHARACTERISTICS

### 4.1. Energy gap of $\text{Si}_6\text{H}_{12}$

Figure 4(a and b) shows  $(dI/dV)/(I/V)$  spectra measured on isolated  $\text{Si}_6\text{H}_{12}$  clusters. The gap of electron states is clearly seen in cluster spectra (curves a and b). In contrast, in the rest-atom position (curve c), the spectrum shows metal-like behavior, and a peak near -0.7 eV is attributed to rest-atom surface states, which is consistent with the literature.[6] The measured gap of isolated clusters located at a center of the faulted half is larger than 1.5 eV (curve a), while for clusters shifted to a corner adatom the gap is smaller than 1 eV (curve b). The cluster height measured from STM images is 0.1-0.2 nm for the centered clusters and 0.22-0.35 nm for the shifted ones. The gap is large for the s-

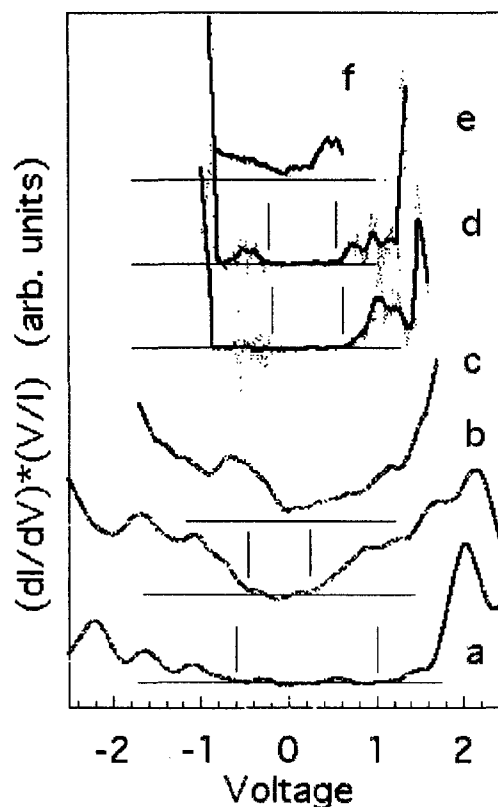


Figure 4: STS spectra of isolated  $\text{Si}_6\text{H}_{12}$  (a and b) and  $\text{Si}_8\text{H}_{18}$  (d-e) clusters. (c) is an unreacted rest-atom spectrum, and (f) for (2x1) array of  $\text{Si}_8\text{H}_{18}$ .

mall cluster height and correlates the cluster position in the (7x7) unit cell.

The observation of position-dependent characteristics indicates that cluster-substrate interaction plays a role to modify STS spectra of  $\text{Si}_6\text{H}_{12}$  clusters. When the cluster is centered, resonance tunneling through molecular cluster levels causes tunneling current measured by STM.[7] Thus, the broad peaks at about +2 V and -1 V (Fig. 4 (a)) are associated with the LUMO and HOMO states of  $\text{Si}_6\text{H}_{12}$  clusters. Broadening may result from interaction with the substrate. When the cluster is shifted, the increase in tunneling current is due to mixing of the cluster orbital and the surface states and thus lowering of the tunneling barrier. The effect, discussed by Eigler et. al.[8] for Xe atoms adsorbed on Ni(110), led to a significant enlarge of the tunneling current at Xe position. For the shifted clusters, the mixing of electron states leads to the smaller gap observed in STS spectra since the clusters stay over a rest-atom dangling bond.

#### 4.2. $\text{Si}_8\text{H}_{18}$ cluster gap

STS spectra measured on isolated  $\text{Si}_8\text{H}_{18}$  clusters show a smaller gap than that observed on the  $\text{Si}_8\text{H}_{12}$  clusters. The gap is  $\sim 0.8$  eV (curves d and e), while no gap was observed on the (2x1) array (curve f). STS spectra show clear difference between these two types of clusters. The observation of smaller gap for the (n=8) clusters is in general agreement with the theoretical prediction of smaller HOMO-LUMO gap when the number of Si atoms increases. When the clusters are adsorbed on the surface in an array, the cluster-substrate and cluster-cluster interactions alter the local properties resulting in the metal-like conductance observed on the (2x1) array. Detailed theoretical calculations of electron states for the cluster adsorbed on the surface will be needed to clarify the origin of observed spectral features.

### 5. CONCLUSION

Adsorption and electronic characterization of the hydrogen-saturated Si clusters deposited on Si(111)-(7x7) surfaces were investigated by STM/STS. Converted from the cluster ions by losing a hydrogen atom, the neutral  $\text{Si}_n\text{H}_x$  (n=6, x=12 and n=8, x=18) clusters are physically adsorbed on the Si(111)-(7x7) surface. Different structures were observed depending on the cluster type and the deposition energy. The STS spectra measured on isolated clusters show the energy gap larger than 1.5 eV for  $\text{Si}_6\text{H}_{12}$  and about 1 eV for  $\text{Si}_8\text{H}_{18}$ , while no gap is observed on the (2x1) cluster array. The results demonstrate that electronic characteristics of deposited clusters depend on the cluster type and the local arrangement.

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